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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The major objective of this project was to develop theoretical models and techniques for describing vibrational relaxation in molecular collisions at low temperatures. If attractive forces are sufficiently strong, the colliding molecules can form a weakly bound complexes. Models have been developed to provide both a quantitative and a qualitative interpretation of the mechanisms and dynamics of intercomplex energy transfer processes. The processes considered in the investigation are; DF(v=1) + DF(v=0), H ₂ O(010) + H ₂ O(000), D ₂ O(010) + (continued on reverse side)		

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+ $D_2O(000)$, and $HCl(v=1) + Cl$. The investigation included the determination of energy levels of newly formed bonds and internal oscillatory motions. In addition, the following aspects of molecular collisions have also been investigated; vibration-vibration energy transfer in $CO_2(00^0_1) + H_2/D_2$, F-atom deexcitation of $DF(v=1)$, approximate solution of the time-dependent Schrödinger equation for vibration-vibration energy transfer, and exact quantum mechanical treatment of vibration-translation energy transfer employing a step potential.

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Reno, Nevada 89557
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2. PRINCIPAL INVESTIGATOR: Professor H. K. Shin

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8. PUBLICATIONS:

"F-Atom Deexcitation of $DF(v=1)$: Isotope Effect", H. K. Shin, Chem. Phys. Letters, 46, 260 (1977).

"Determination of Vibrational Energy Level Spacings of van der Waals Molecules from the Lennard-Jones Potential", H. K. Shin, Chem. Phys. Letters, 47, 225 (1977).

"Vibrational Relaxation of H_2O at High Temperatures", H. K. Shin, J. Phys. Chem., 81, 1122 (1977).

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"A Model Calculation of Vibration-Translation Energy Transfer", P. L. Altick and H. K. Shin, J. Chem. Phys., 68, 3973 (1978).

"Transfer of Vibrational Energy to Oscillatory, Restricted Rotational and Translational Motion in $HCl + Cl$ ", H. K. Shin, J. Chem. Phys., 68, 5265 (1978).

"Vibrational Relaxation of Water Molecules near Room Temperature", H. K. Shin, J. Chem. Phys., in press.

"Molecular Energy Transfer Studies", H. K. Shin, Final Technical Report.

In preparation:

"Deexcitation of $D_2O(010)$ near Room Temperature", Y. H. Kim and H. K. Shin

"Vibrational Relaxation of Diatomic Molecules in Condensed Monatomic Media", H. K. Shin

"Vibrational Relaxation of van der Waals Molecules", H. K. Shin

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The major concern has been with vibrational energy transfer in molecular collisions involving hydrogen halides and water molecules at low temperatures. As the temperature of the collision system is lowered, the reduction of thermal energy leads to the appearance of a number of interesting phenomena that are obscured or nonexistent at higher temperatures. One such phenomenon, which is of particular importance to the study of molecular energy transfer is the manifestation of intermolecular attraction. When the colliding molecules approach each other at low temperatures they spend more time in those orientations for which the attraction is strong. If attractive forces are sufficiently strong ($E_{\text{attr}} \gg kT$), the colliding molecules can form a weakly bound complexes. In collision systems involving vibrationally excited molecules, the formation of such a complex can lead to efficient relaxation through intracomplex energy transfer. Since the subunit molecules cannot undergo free translation and/or rotation, conventional vibration-translation and/or vibration-rotation energy transfer theories are no longer useful, and new theories will have to be formulated. During the support period, we have developed such a theoretical approach recognizing the formation of loosely bound complexes.

To understand the details of energy transfer processes in the complex, it is essential to determine energy levels of the newly-formed bond. An analytical approach to determine the levels by use of the Lennard-Jones potential in the WKB method has been developed. Specific systems considered are rare gas molecules and argon-hydrogen halide complexes. The former molecules are chosen to establish the method since experimental data are available for them. We have determined spectroscopic constants and energy levels of the bond of all these molecules and complexes, and found that results are in good agreement

with experimental data. We have also predicted values of such constants for complexes for which no experimental data are available.

Energy transfer probabilities of $DF(v=1) + DF(v=0) \rightarrow 2 DF(v=0)$ in the temperature range of 200 - 400°K have been calculated recognizing the presence of strong attractive forces and formation of a DF dimer. Probabilities are large and exhibit a sharp negative temperature dependence below 300°K, the result which can be attributed to the transfer of energy to the oscillatory motion of DF in the dimer. The model has also been used to study the vibrational relaxation of $H_2O(010)$. Large values of the ν_2 -deexcitation probability found near room temperature are incompatible with earlier sound-absorption data, but are in agreement with recent results obtained with laser excited fluorescence techniques. At present experimental data on the ν_2 -deexcitation of $D_2O(010)$ are not available, but the present model gives deexcitation probabilities which are somewhat smaller than that of H_2O over the temperature range of 200 - 400°K. Another system investigated based on the complex formation is $HCl(v=1) + Cl$. The attractive energy between the colliding partners is significantly less than that of DF or H_2O , but the energy transfer can be explained in terms of the model.

The model described above works for low-temperature relaxation processes. As the temperature increases, the role of weakly bound complexes becomes less important and an entirely different model will have to be used. The change in energy transfer mechanism has been demonstrated for $H_2O(010)$ calculating deexcitation probabilities over 1000 - 4000°K by use of vibration-rotation energy transfer theory. Probabilities are found to be large and are comparable to that at temperatures near 300°K obtained with the model of complex formation. The comparison shows the appearance of a probability minimum near 600°K.

We have investigated intramolecular vibration-vibration energy transfer in $\text{CO}_2(00^{\circ}1) + \text{H}_2/\text{D}_2$ to determine the most efficient energy transfer pathway. Over the temperature range of 100 - 2500°K, the intramolecular process $(00^{\circ}1 \rightarrow 10^{\circ}0)$ is found to be the dominant process in both collision systems. Another system investigated is the F-atom deexcitation of $\text{DF}(v=1)$. Near room temperature, the deexcitation rate constant is small but increases rapidly with increasing temperature. It is also found that the system relaxes faster than $\text{HF} + \text{F}$ over the temperature range of 100 - 3000°K.

An approximate solution of the time-dependent Schrödinger equation was developed for vibration-vibration energy transfer in a collinear collision of two diatomic molecules. This work has been undertaken to obtain the solution for an arbitrary form of interaction potential. Also undertaken is a full quantum mechanical treatment of vibration-translation energy transfer in an atom-diatom collinear collision employing a simple step potential for which the resulting coupled differential equations were solved exactly.